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(54) HYDROGEN STORAGE BY REVERSIBLE HYDROGENATION OF PI-CONJUGATED SUBSTRATES

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(56) References Cited

U.S. PATENT DOCUMENTS

4,567,033	\mathbf{A}	1/1986	Kesten
5,197,523	A	3/1993	Fink, Jr. et al.
5,435,356	A	7/1995	Rabinovich
6,074,447	A	6/2000	Jensen
6,544,400	B2	4/2003	Hockaday et al.
6,607,707	B2 *	8/2003	Reichman et al 423/648.1
6,680,042	B1*	1/2004	Schulz et al 423/644
2001/0016283	$\mathbf{A}1$	8/2001	Shirashi et al.
2002/0096048	$\mathbf{A}1$	7/2002	Cooper et al.
2005/0002857	A1*	1/2005	Pez et al 423/648.1

FOREIGN PATENT DOCUMENTS

JР	2001110437 A	4/2001
JP	2001198469 A	7/2001
JР	2002134141 A	5/2002
JP	2002184436 A	6/2002
JP	2002-194436	7/2002
JP	2002187702 A	7/2002
JP	2002274803 A	9/2002
JP	2002274804 A	9/2002
JP	2003321201 A	11/2003
JP	2004026582 A	1/2004

12/2000

5/2002

6/2005

Dillon, et al., "Storage of Hydrogen in Single-Walled Carbon Nanotubes", *Letters to Nature*, Mar. 27 2997, vol. 386, pp. 377-379.

OTHER PUBLICATIONS

Chambers, et al., "Hydrogen Storage in Graphite Nanofibers", *The Journal of Physical Chemistry B*, May 28, 1998, vol. 102, No. 22, pp. 4253-4256.

Cho, et al., "Hydrogen Sorption in HCI-Treated Polyaniline and Polypyrrole"; New Potential Hydrogen Storage Media, *Fuel Chemistry Division Preprints*, 2002, 47(2), pp. 790-791.

Kariya, et al., "Efficient Evolution of Hydrogen from Liquid Cycloalkanes Over Pt-containing Catalysts Supported on Active Carbons Under Wet-Dry Multiphase Conditions", *Applied Catalysis A: General*, 233 (2002), pp. 91-102.

Loutfy, et al., "Investigation of Hydrogen Storage in Liquid Organic Hydrides", Proceedings of the *International Hydrogen Energy Forum 2000*, Munich Germany, 2000; pp. 335-340.

Dillon, et al., "Hydrogen Storage Using Carbon Adsorbents: Past, Present and Future", *Applied Physics A*, 72 (2001), pp. 133-142.

Hodoshima, et al., "Liquid-film-type Catalytic Decalin Dehydrogeno-aromatization for Long-term Storage and Long-distance Transportation of Hydrogen", *International Journal of Hydrogen Energy*, 28 (2003), pp. 197-204.

"Conducting Plastics Pack the Hydrogen", *Science*, vol. 297, Sep. 13, 2002, p. 1796.

(Continued)

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(57) ABSTRACT

Processes are provided for the storage and release of hydrogen by means of a substantially reversible catalytic hydrogenation of extended pi-conjugated substrates which include large polycyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons with nitrogen heteroatoms, polycyclic aromatic hydrocarbons with oxygen heteroatoms, polycyclic aromatic hydrocarbons with alkyl, alkoxy, nitrile, ketone, ether or polyether substituents, pi-conjugated molecules comprising 5 membered rings, pi-conjugated molecules comprising six and five membered rings with nitrogen or oxygen hetero atoms, and extended pi-conjugated organic polymers. The hydrogen, contained in the at least partially hydrogenated form of the extended pi-conjugated system, can be facilely released for use by a catalytic dehydrogenation of the latter in the presence of a dehydrogenation catalyst which can be effected by lowering the hydrogen gas pressure, generally to pressures greater than 0.1 bar or raising the temperature to less than 250° C. or less, or by a combination of these two process parameters.

62 Claims, 19 Drawing Sheets